

SCIENCE FOR CERAMIC PRODUCTION

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HYBRID SOL – GEL METHOD OF OBTAINING NANOSTRUCTURED YTTRIUM-ALUMINUM GARNET POWDERS FOR LASER CERAMIC

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The production of finely dispersed yttrium-aluminum garnet (YAG) powder, which is the initial material for ceramics, using as precursors secondary aluminum butylate and a crystal-hydrate salt — yttrium chloride hexahydrate, is examined. It is found that depending on the conditions of synthesis and temperature solid products of different forms are formed. The conditions for synthesizing the crystalline phase of YAG by heat-treatment of the precipitates obtained at temperature $\geq 900^\circ\text{C}$ are determined.

Key words: sol – gel method, hybrid method, semialkoxide method, yttrium-aluminum garnet.

On account of its optical and thermo-mechanical properties yttrium-aluminum garnet (YAG) is widely used as a crystal base for making many laser materials. The structure of YAG makes it possible to introduce diverse rare-earth ions and iron-group ions as dopants into it.

The most widely used method of obtaining a YAG mix for growing single crystals is solid-phase synthesis. The YAG mix is also obtained by precipitation in the form of oxalates, carbonates, and hydroxides followed by treatment at high temperatures. The method of “freezing out” (cryochemical method) and self-propagating high-temperature synthesis are used less often. The sol – gel method is one of the methods being actively developed in recent years for obtaining the YAG mix [1]. At the same time the use of such mixes in complicated and expensive methods for growing refractory crystals from melt does not always give the required optical quality and perfection of laser materials.

The successful realization of a YAG : Nd laser with an active element consisting of transparent ceramic showed real prospects for obtaining a laser ceramic. A highly transparent ceramic YAG : Nd with large size and optical quality exceeding that of the corresponding single crystals was synthesized in [2]. Lasers with active elements consisting of such a ceramic make it possible to obtain record high power, reaching many tens of kilowatts [3].

The development of an ultradispersed materials technology using the sol – gel method [4, 5] is of special interest for making highly transparent laser ceramic. The fundamental achievement of this technology lies in the possibility of monitoring the interphase surface of the material at a very early stage of its production and creating a unique homogeneous structure or structures with an ultradisperse phase [6]. The main advantages of the sol – gel technology as compared with other methods are the more uniform distribution of additives, higher dispersity of the powders obtained, and others. The distribution of the precursors in the porous matrix when using the sol – gel method for synthesis of disperse systems creates an effective barrier for agglomeration processes and makes it possible to maintain nanosize particles in a high-temperature processing regime. As a rule the materials and articles obtained are of higher quality as compared with materials fabricated by other methods [4, 5, 7].

Our work is devoted to an investigation of the production of nanostructured YAG powder by a hybrid sol – gel method using a solution of secondary aluminum butylate (SAB) and yttrium chloride hexahydrate. The technology being developed comprises one form of the sol – gel method: the required oxide structure is obtained by chemical interaction of alkoxide and salt components. It is proposed that two classes of chemical reagents — various metal alkoxides and salts — be used as the initial material for synthesis of complex oxide structures. This makes it possible to search for optimal combinations of the initial materials and methods of hydrolysis as well as possible solutions for technical problems, such as

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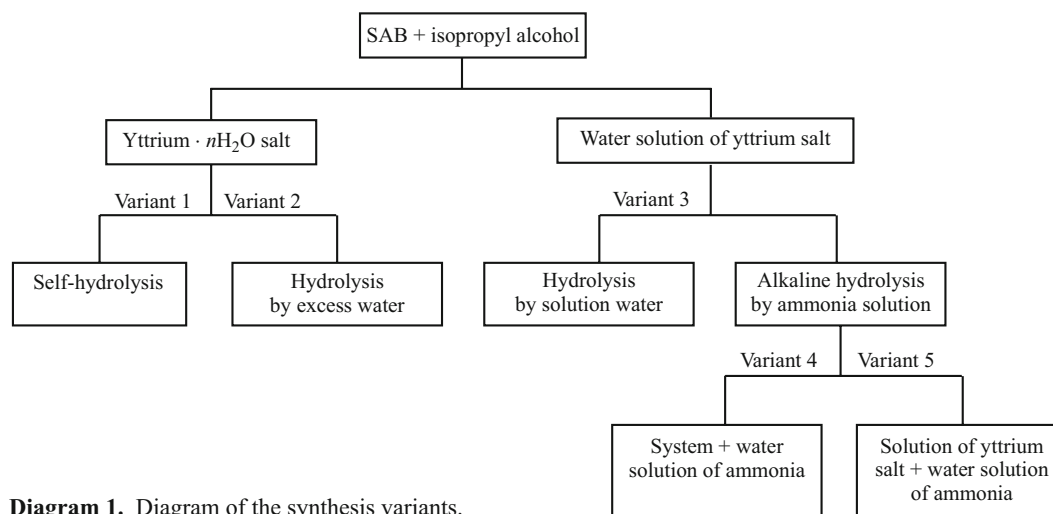


Diagram 1. Diagram of the synthesis variants.

lowering the sintering temperature of the oxide compositions. The hybrid variant of the sol – gel method combines the main advantages of alkoxide (possibility of additional purification, monitoring the interphase surface and particle size at the hydrolysis stage, and others) and salt (low cost, operational simplicity, precise concentration control, and others) methods and is most promising.

The sequence in which the components are introduced affects the tendency of the particles to form agglomerations. The system possesses high acidity after yttrium salt is introduced into the solution (SAB + isopropyl alcohol). These conditions promote a stable ultradisperse state with minimal tendency of the particles toward agglomeration. For this reason there is no need for further “acidification” of the sol at the early stages of its formation. Alkaline hydrolysis displaced the equilibrium toward agglomeration and growth of crystalline particles. The morphology and size of the particles depend not only on the type of alkoxo compounds, solvent, and reaction temperature but also on the initial concentration of the hydrolyzing water solution of ammonia.

The method of hydrolysis has a strong effect on the shape and size of the sol particles as well as on their tendency toward agglomeration during subsequent heat treatment. For this reason the effect of the conditions of hydrolysis with the solution introduced into system formed and simultaneously with the introduction of a salt solution was examined.

Five variants of yttrium introduction (see Diagram 1) were implemented:

in the form of salt, hydrolysis due to water of crystallization (self-hydrolysis);

in the form of salt, hydrolysis by introduction of excess water;

in form of a water solution of a salt, hydrolysis by solution water;

in the form of a water solution of a salt, alkaline hydrolysis;

in the form of a water solution of a complex compound with ammonia, hydrolysis by solution water.

The solid products formed during hydrolysis were dried at temperature 70 – 80°C, and the xerogel formed was subjected to two-stage sintering at the temperatures 650°C (stage I) and 900°C (stage II). The sintering time at stages I and II varied and was equal to 2, 4, and 6 h. The dependences of the yield of the required phase (YAG) on the temperature and heat-treatment time as well as the effect of the temperature, duration, and number of sintering cycles on the behavior of the particles formed during hydrolysis were determined. The powders were investigated by XPA and electron microscopy.

Variant 1. Complete or partial self-hydrolysis occurred when yttrium was introduced in the form of a crystal-hydrate of a salt. If the amount of water was close to the amount theoretically required for complete hydrolysis, the system developed according to the scheme solution – sol – gel – (drying) – xerogel – (sintering) – powder. When the amount of the water of crystallization is much greater than required, as in the case where yttrium chloride hexahydrate salt is used, the system transformed from a solution into a state with a thick suspension and the sol – gel transition stage could not be clearly identified.

The samples obtained at stage I sintering contained a large amorphous part irrespective of the soaking time; this is due to incomplete particle formation. The degree of amorphousness decreased during stage II heat-treatment. As the duration of stage I increased from 2 to 6 h the degree of the amorphousness decreased but in the process the YAG yield decreased to 10%. When the heat-treatment time at stage II increased from 2 to 6 h and the soaking time at stage I was the same, the yield of the YAG crystal phase increased to 81 – 94%.

Variant 2. The processes in which excess water was added after powder of the salt was introduced into the system were conducted according to a similar scheme under the same conditions. In this case a suspension formed more in-

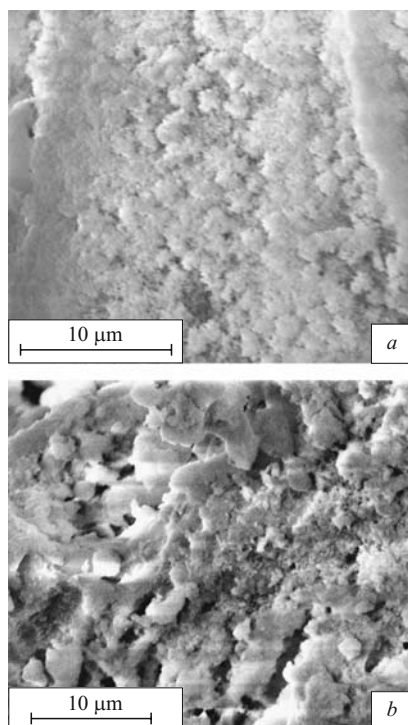


Fig. 1. Electron-microscopic photographs of samples with minimal (*a*, soaking time at stage I and II sintering is 2 h) and maximal (*b*, soaking time at stage I and II sintering is 6 h) heat-treatment times.

tensively than in the preceding case; this is due to the introduction of additional hydrolyzing agent.

After stage I sintering yttrium oxide was the only crystalline phase manifesting. The degree of amorphousness of the product decreased after stage II heat treatment. When the duration of the stage I sintering increased with the same soaking time at stage II the degree of amorphousness decreased sharply, and the YAG yield increased to 40 – 60%. When the duration of stage II increased with the same soaking time at stage I the product yield increased by 10% on average. This attests to the formation of a highly concentrated system where conditions for intense coagulation of the particles and more active particle growth are created. A $Y_4Al_2O_9$ phase appeared in all cases; its content decreased when the heat-treatment time increased. The content of the YAG phase did not exceed 60% on average.

Variant 3. The introduction of yttrium in the form of saturated water solution of a salt with hydrolysis by excess water occurred simultaneously with the formation of product with stoichiometric composition. The use of yttrium chloride hexahydrate salt made it possible to conduct the synthesis as mixing of two uniform solutions, which facilitates the homogenization of a system in which sol- and gel-formation occur simultaneously.

After stage-I sintering the samples were identical to those obtained in the preceding variant of synthesis. For minimum soaking time at stage I the amorphous part completely vanished; this is probably due to more complete and

uniform hydrolysis. Increasing the duration of stage I with the same soaking at stage II from 2 to 6 h increased the YAG yield from 30 – 70 to 90 – 100%. When the duration of stage II was increased from 2 to 6 h the YAG yield increased from 30 to 100%. The secondary crystalline phases $YAlO_3$ and $Y_4Al_2O_9$ were observed in all samples which had undergone primary sintering. In the process of sintering at 900°C for 4 h the content of these phases in certain cases exceeded 50%. In summary, under the conditions of synthesis and sintering examined the YAG yield fluctuated in the range 22 – 100%.

Variants 4 and 5. When yttrium was added in the form of a water solution of a salt and alkali hydrolysis was used the condition for ultraexcessive water hydrolysis was realized. A solution containing yttrium salt and ammonia was prepared beforehand. Since the salt forms a complex compound with ammonia, a transparent colloid formed first; this colloid was driven into a state of a homogeneous solution by intense mixing, after which the two solutions (aluminum- and yttrium-containing) were mixed by intense mixing.

In the case of alkali hydrolysis the YAG phase already appeared after the first sinter. For intermediate soaking times the secondary phases $YAlO_3$ and $Y_4Al_2O_9$ formed. The degree of amorphousness decreased after stage II of heat treatment. When the duration of stage I was increased with the same soaking time at stage II the YAG yield increased from 30 to 80%. When the soaking time at stage II was increased from 2 to 6 h the YAG yield increased from 30 – 60 to 70 – 90%. The $YAlO_3$ phase is characteristic for all samples obtained with alkali hydrolysis. Its content with yttrium introduced in the form of a water solution of the salt followed by alkali hydrolysis reached 75%. For synthesis with yttrium introduced simultaneously in the form of a water solution of a complex compound with ammonia some samples contained secondary products — $YAlO_3$ and $Y_4Al_2O_9$ (no more than 20%), but no regularity in their appearance was found. The YAG yield in this case did not exceed 80%.

Comparing the XPA data obtained for different variants of synthesis and heat-treatment regimes with one another, it can be concluded that only the system with a water solution of the yttrium salt with medium temporal regimes of heat-treatment gives 100% yield of the YAG phase. At the same time systems formed when yttrium is introduced in the form of a crystal hydrate of the salt give the lowest YAG yield. For alkali hydrolysis, depending on the temperature – time regime, a high yield of the required phase can be obtained but then a secondary phase is always present.

The electron-microscopic investigations of the powders obtained make it possible to draw a number of conclusions which are important for understanding the particle transformation processes as a function of the sintering time and temperature as well as the effect of the form of the hydrolysis on the character of particle agglomeration during heat-treatment.

In the case of rapid sintering (Fig. 1) the particles formed are shapeless or are nearly spherical, but their size fluctuates over a wide interval — from 150 to 650 nm. However, there

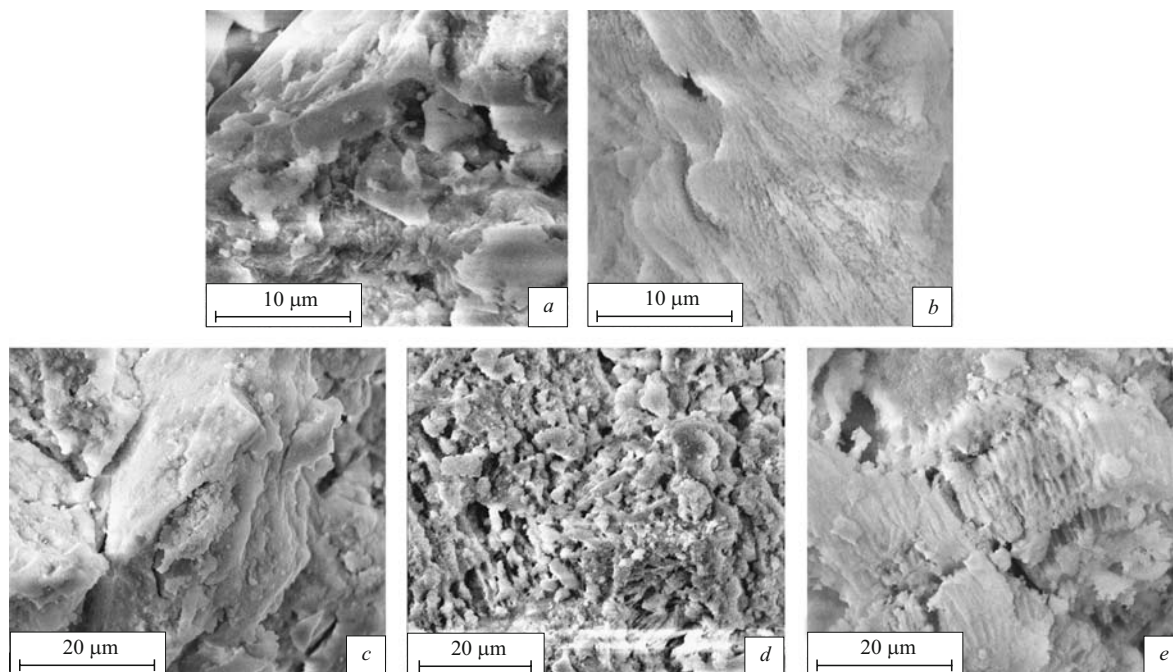


Fig. 2. Electron-microscopic photographs of samples obtained as a result of hydrolysis: *a*) self-hydrolysis (variant 1); *b*) hydrolysis by excess water (variant 2); *c*) hydrolysis by solution water (variant 3); *d*) alkali hydrolysis (variants 4 and 5).

are grounds for believing that these structures consist of smaller agglomerates and particles which fall into the nanometer range (smaller than 100 nm) and therefore nanostructured formations appear. For longer secondary sintering times, the particle-size range shrinks. The particles form agglomerates, in most cases retaining their previous shape. The average size of the agglomerates is 6 μm , and they in turn form even large agglomerates. As a result of sintering at low temperatures and short-time heat-treatment agglomerates with a loose structure are formed, and they become denser when the duration and temperature increase.

The character of the hydrolysis has a large effect on not only the particle formation process but especially on the subsequent self-organization of the particles (Fig. 2). Comparing the samples differing only by the method of hydrolysis but with the same soaking time at stages I and II of heat-treatment, one can see in the sequence self-hydrolysis – excess-water hydrolysis – solution-water hydrolysis – alkali hydrolysis a dependence of the change of the structure of the agglomerates from a distinct layered to fine-columnar structures, which, in turn, consist of smaller spherical agglomerates.

In summary, nanostructured yttrium-aluminum-garnet powders were obtained by a hybrid sol – gel method from secondary aluminum butylate using a different sequence for introducing the components and different methods of hydrolysis and varying the sintering conditions.

When yttrium was introduced into the system SAB – isopropyl alcohol in the form of a water solution of a salt, YAG yield close to 100% was obtained.

For rapid primary sintering (2 h) the YAG particles formed exhibit a wide range of sizes, ranging from 150 to 650 nm. When the duration of the secondary sinter is increased (to 4 – 6 h) the particles grow together into loose agglomerates approximately 6 μm in size.

The hydrolysis method affects the degree of particle agglomeration as well as the structure of the agglomerates, which changes from layered to fine-columnar in the sequence self-hydrolysis – excess-water hydrolysis – solution-water hydrolysis – alkali hydrolysis.

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